

Critical behaviour of stiff polymer near the surface

Debaprasad Giri*, P K Mishra† and Sanjay Kumar†

Centre for Theoretical Studies, Indian Institute of Technology Kharagpur, Kharagpur-721 302, West Bengal, India

†Department of Physics, Banaras Hindu University, Varanasi-221 005, Uttar Pradesh, India

E-mail : giri@cts.iitkgp.ernet.in

Abstract : We use the self-avoiding walk models to investigate the adsorption transition of semi-flexible homopolymer chain in two and three dimensions. The exact-enumeration method has been used to locate the transition points. The results obtained from this method have been compared with the exact results found for the directed walk model of semi-flexible polymer.

Keywords : Semi-flexible polymer, adsorption, stiffness.

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Biopolymers (e.g. polysaccharide, DNA, protein and many others) play an important role in biological phenomena. These phenomena are associated with the structure of the chain or flexibility of the chains [1,2,3]. For example, protein folding is the phenomena which is associated with the primary structure of the chain. On the other hand, stiffness plays an important role in the DNA denaturation. If stiffness is small, persistence length associated with the chain is much smaller than the overall length of the chain and chain is said to be flexible. When stiffness is large and persistence length being comparable to the chain length, the chain is said to be rigid. If stiffness is intermediate, the chain is said to be semi-flexible. Few important examples from biology are actin filaments, microtubules, DNA and collagen. Since the free rotation about the chain backbone are restricted, the usual chain statistics can not be described by the conventional models describing the flexible chain.

An impenetrable surface is known to affect the conformational properties of polymer chain. This is due to subtle competition between the gain of internal energy and corresponding loss of entropy at the surface. Since the rigidity of the chain reduces the entropy, a semi-flexible chain is expected to show different adsorption behaviour. Few attempts have recently been made to describe the adsorption of semi-flexible [4,5,6,7] polymer chain at surface. Kramarenko *et al* [6] while discussing adsorption of flexible

polymer chain on impenetrable surface using molecular dynamic simulation showed that adsorption characteristics are changed by varying the degree of stiffness. The universal behaviour associated with the semi-flexible polymer is still unclear. For example, the number of monomers on the surface N_s at the transition point scales as

$$N_s \sim N^\Phi, \quad (1)$$

where Φ is a crossover exponent. Sintes *et al* [7] showed through numerical simulation that the critical exponents for the semi-flexible chain belong to the same universality class as that of the flexible polymer chain.

In this paper we study the self-avoiding walk model of a linear polymer chain on a lattice and interacting with the impenetrable surface. Any turn in the walk cost energy, representing reduction in the stiffness of the chain. The analytical approaches are limited to very few cases such as directed walks or worm like chain (WLC) model of semi-flexible polymer [8]. Although the WLC model has been used extensively to study the conformational properties and surface adsorption transition of a semi-flexible chain, however, it can not mimic exactly the dimensional behaviour of the real chains [9]. On the other hand directed walk model is too simplistic model to study the qualitative behaviour. Therefore, we prefer numerical methods to study

*Corresponding Author

the phase diagram of surface interacting semi-flexible polymer. A lattice model using extrapolation of exact series expansions (herein after referred to exact enumeration technique) has been found to give satisfactory results as it takes into the account the correction to scaling. To achieve the same accuracy by Monte Carlo method, a chain of about two order magnitude larger than the exact enumeration is needed [10]. In a recent paper by Mishra *et al* [4], it was shown that the result obtained from exact enumeration technique is in excellent agreement with the exact results obtained for directed walk model of semi-flexible polymer chain interacting with the surface.

Let $C_N(N_s, N_b)$ be the number of SAWs having N_s monomers on the surface and N_b number of bends in the chain. We analysed the series for $C_N(N_s, N_b)$ upto $N = 28$ for the square lattice and $N = 18$ for the cubic lattice respectively. The partition function of our interest is

$$Z_N(\omega, b) = \sum_{N_s, N_b} C_N(N_s, N_b) \omega^{N_s} b^{N_b}, \quad (2)$$

where $\omega = e^{-\beta \epsilon_s}$ and $b = e^{-\beta \epsilon_b}$ are the Boltzmann weight associated with each step on the surface and every turn associated with the chain respectively. Here, β is the inverse temperature. The reduced free energy per monomer is found from the relation

$$G(\omega, b) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N(\omega, b). \quad (3)$$

$Z_N(\omega, b)$ is calculated from the data of $C_N(N_s, N_b)$ using equation (1) for a given value of ω and b . To extrapolate to large N , ratio method [11] has been used. The resultant phase diagram is shown in Figure 1.

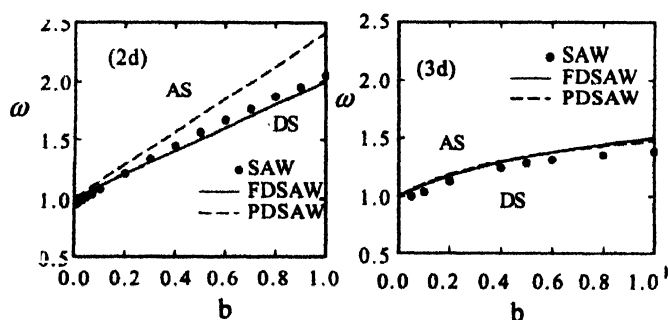


Figure 1. This phase diagram shows variation of ω with b in 2d and 3d respectively. For comparison exact phase boundary for FDSAW and PDSAW has also been shown by full line and broken line respectively.

We have also calculated various physical quantities of interests *e.g.* persistence length (l_p), average number of monomers on the surface ($\langle N_s \rangle$), average number of

bends ($\langle N_b \rangle$) in the chain by the following relations

$$l_p = \frac{N}{\langle N_b \rangle}; \quad \langle N_b \rangle = b \frac{\partial G}{\partial b}; \quad \langle N_s \rangle = \omega \frac{\partial G}{\partial \omega} \quad (4)$$

The variation of $\langle N_s \rangle$ with ω and b is shown in Figure 2.

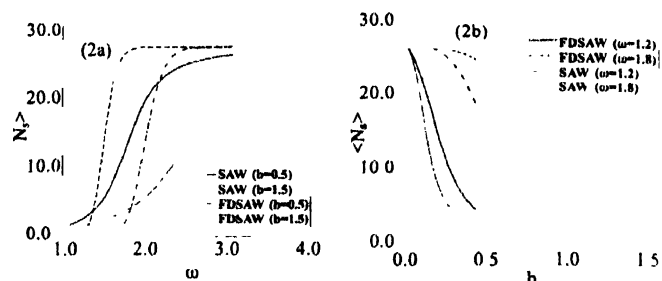


Figure 2. Diagram shows variation of $\langle N_s \rangle$ with ω and b respectively

Following conclusions can be easily drawn from the Figures 1-3. The adsorption transition takes place at higher temperature for semi-flexible chain compare to the flexible chain [4,7]. For flexible chain $b = 1$, ω_c is found to be equal to 2.05 ± 0.01 for 2d and 1.38 ± 0.01 for 3d [12]. For $b < 1$ ω is found to be less than ω_c indicating the higher adsorption temperature. This is because of restricted rotations, stiffer chain losses entropy compared to flexible chains while adsorbing on the surface. In Figure 1 we have also plotted the exact phase diagrams for Fully Directed Self Avoiding Walks (FDSAW) and Partial Directed Self Avoiding Walks (PDSAW). The adsorption transition for FDSAW and SAW are very close to each other while differ from PDSAW for any value of b except $b = 0$. This is because of the choice of the adsorbing surface along the preferred direction, which causes asymmetry in the problem.

In this calculation, we have found that average number of monomer adsorbed on the wall decreases with increase of b as shown in Figure 2. However, crossover exponent ϕ is found to be 0.5 ± 0.03 for $b = 0.9, 1.0$ and 1.1 . This may be understood from the fact that bending is local phenomena and does not affect the universality of the system.

The behaviour of persistence length with b is shown in Figure 3. As b decreases persistence length increases, it is therefore, difficult to predict the value of ϕ at lower values of b . The persistence length diverges with decrease of b indicating the transition from flexible to rigid rod is of first order. In the limit $b \rightarrow 1$, the persistence length approaches 1.6 which may be compared to the limiting value of l_p , 2 and 1.75 for FDSAW and PDSAW respectively. For FDSAW (2D) there are only two directions

in which walker can take steps while for PDSAW there are three possibilities. In SAW a walker have all the four choices therefore l_p is found less than FDSAW and PDASW.

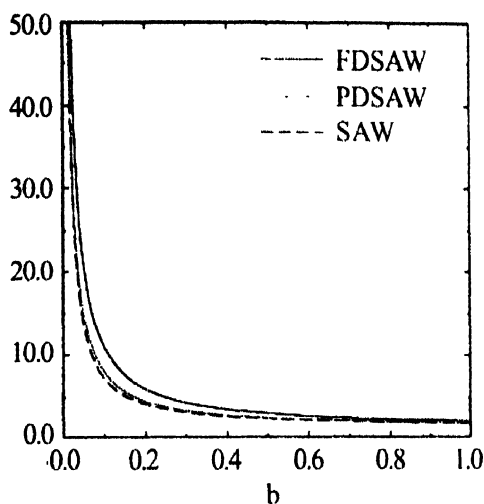


Figure 3. Diagram shows the variation of l_p with b .

Finally, we would like to make a comment that series expansion technique may not give correct results for lower values of b which effectively reduces the chain length.

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